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(54) Title: ANTI-FOAM MATERIAL

(57) Abstract

A granular anti-foam material, preferably for detergent compositions, and compositions containing such a material. The anti-foam material comprises a carrier, e.g. a zeolite, a silicone anti-foam agent, and a fatty acid ester of a polyhydric alcohol, e.g. sorbitan monooleate. The anti-foam material may additionally contain a silicate.

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ANTI-FOAM MATERIAL

This invention relates to granular materials and more especially to a particulate anti-foam material for use in powdered or granular detergent compositions.

Granular materials for a wide range of purposes are often prepared from an absorbent carrier material and a liquid. However, it is difficult to produce granules of adequate strength and if the granules disintegrate they tend to cake, and they may also cause caking of any other particulate material to which they may be added.

Silicone anti-foam agents are widely used, but when incorporated into anti-foam materials, their performance tends to deteriorate on prolonged storage. Attempts to overcome this have included encapsulating the silicone anti-foam agent by the addition of an organic alcohol or wax, but these proposals have not always proved satisfactory.

According to the present invention, we provide a granular anti-foam material comprising a carrier, a silicone anti-foam agent, and a fatty acid ester of a polyhydric alcohol.

Preferably the anti-foam material is for detergent compositions.

Preferably the granular anti-foam material additionally comprises a silicate.

The granular anti-foam material includes a fatty acid ester of a polyhydric alcohol in order to overcome the problem of deterioration of the anti-foam material on storage, and preferably a silicate to increase granule strength. The granules may be provided with a surface coating of aluminosilicate dust. Preferably the silicate is soluble.

The silicone anti-foam agent may be one of those conventionally used in detergent compositions.

The fatty acid ester combats the problem of deterioration in the performance of the anti-foam material on storage. The ester acts as a form of encapsulant this leading to a granule with lower susceptibility to degradation by surfactant.

The fatty acid component of the ester is preferably unsaturated. A C_{10} to C_{26} unsaturated fatty acid is preferably used. Oleic acid (C_{18}) is especially preferred. The polyhydric alcohol is preferably a triol, more preferably sorbitol.

The ester is preferably liquid at ambient temperature. It preferably has an HLB value of 2-7, more preferably 4-5.

A particularly preferred ester is sorbitan monooleate which has an HLB value within the range mentioned in the preceding sentence.

A wide range of absorbent carrier materials may be used. Inorganic materials include zeolites, such as zeolite

A, and organic materials include cellulose-based products such as corn husk powder. The silicate preferably has a ratio of 1.5 to 2.5 and may be sodium disilicate.

We have found, surprisingly, that addition of silicate increases significantly the strength and hardness of the granules, enabling the proportion of carrier to be reduced. This is particularly important where the active component in the granular material is comprised by a liquid. There is a preferred optimum silicate addition level is about 1-25% by weight of the final composition, especially 8-14% by weight which is required to produce a granule that does not cake yet disperses readily. Too much silicate reduces dispersion, too little silicate produces a granule which cakes. Also the silicate level must be balanced to produce a granule which has a low attrition rate on handling. Too little silicate can result in a granule which easily degrades on handling. The optimum concentration of silicate may vary according to the amount of silicate anti-foam and ester used.

Preferably, the anti-foam material contains from 40 to 80% by weight of the aluminosilicate, more preferably about 60%. The aluminosilicate is preferably bentonite or a zeolite, for example zeolite A. The anti-foam material preferably contains roughly similar proportions of the silicone anti-foam agent and the fatty acid ester. Each of these may be either independently or dependently present in

an amount of from 3 to 18% by weight of the whole composition. Each of these two components may, for example be present in an amount of 7% to 11% by weight of the anti-foam material and 7 to 11% by weight of the fatty acid ester, although it may be advantageous to reduce the percentage of fatty acid ester somewhat. Preferably both the silicone anti-foam agent and fatty acid ester are each present in an amount of about 10% by weight.

The aluminosilicate dust applied as a coating to the granules is preferably a zeolite, e.g. zeolite A and is preferably present in an amount of from 3 to 16% by weight of the anti-foam material, more preferably about 10% by weight.

The ester and the silicone anti-foam agent may be mixed together prior to addition of the carrier (e.g. zeolite) or alternatively the ester may be absorbed onto the zeolite or other carrier prior to addition of the silicone anti-foam agent.

The invention also includes detergent compositions containing the granular anti-foam material according to the invention, especially those for use in front loading washing machines.

The invention also provides a method of preparing a granular anti-foam material for detergent compositions comprising the steps of:

mixing a fatty acid ester of a polyhydric alcohol with

a silicone anti-foam agent;

mixing the mixture produced with a carrier, preferably in a high shear mixer such as a KM mixer;

mixing the carrier containing mixture with a silicate in preferably a high shear granulator; and

drying the final product using, for example, a fluid bed dryer.

Alternatively the ester may be blended with carrier prior to adding silicone and mixing in a high shear mixer. The silicate is then added and the product dried as above.

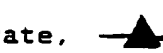
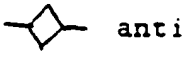
The invention will now be described by way of example with reference to the following figures:

Fig. 1 shows the effect of adding the anti-foam material according to the invention to a first detergent composition (■ with anti-foam material, ◇ without anti-foam material).

Fig. 2 shows the effect of adding the anti-foam material according to the invention to a second detergent composition (■ with anti-foam material, ◇ without anti-foam material).

Fig. 3 shows the effect of components of the anti-foam material on a suds profile for fresh products (◆ no ester, □ no silicate, ▲ no ester or silicate, ◇ anti-foams according to the invention).

Fig. 4 shows the effect of components of the anti-foam material of the suds profile of artificially aged product

( no ester,  no silicate,  no ester or silicate,  anti-foams according to the invention).

EXAMPLES

Example 1

Preparation of anti-foam material

Several batches were made up to form a total premix 5125 grams in weight.

Initially, 62.5 grams of silicone anti-foam (TP 331) and 62.5 grams of sorbitan monooleate (Crill 4) were blended together and the resulting mix was blended with 500 grams of zeolite. This was transferred to a mixer and 784 grams of sodium silicate solution C125 (preheated to approximately 120°C), was sprayed onto the premix via a peristaltic pump and spray nozzle.

The resulting granules were pale yellow in colour, exhibited good granule strength, but had a slight tendency to cake, similar to brown sugar.

98% of the granules would pass through a 10 mesh sieve.

Approximately 3 Kg of the above mixture was sieved at 10 mesh and sprinkled into a fluid bed drier. The granules were dried for approximately 10 minutes at 80°C. During drying the granular strength diminished until the granules disintegrated when touched. Subsequently therefore a further batch of approximately 2 Kg of the original pale yellow granules were sieved at 10 mesh and dried at 30°C for ten minutes, then at 40°C for a further 15 minutes. Granule

strength was better retained in this instance.

It was noted that the material that had been dried at the higher temperature tended to cake more.

The products of both drying experiments were mixed together and dusted with 0.54 Kg of zeolite dust.

A new formulation was made up, as follows:

Zeolite 4000 grams (65%)

TP 331 silicone anti-foam 500 grams (8.2%)

Sorbitan monooleate (Crill 4) 500 grams (8.2%)

Sodium silicate solution (C125) 784 grams (13%)

Zeolite dust (for surface coating) 350 grams (5.6%).

After coating with the zeolite dust and drying the granules were found to be free-flowing and quite strong. The particle size distribution was found to be as follows:

+ 10 mesh (1.7mm)	+ 14 mesh (1.18mm)
0.0	16.0
+ 22 mesh (710µ)	+ 36 mesh (425µ)
53.7	87.1

+ 60 mesh (250µ)	+ 100 mesh (150µ)	- 100 mesh
97.8	99.7	0.3

P = 0.476g cm $^{-3}$

Mean particle size - 730µ

This particle size distribution was found to be ideal for incorporation into a powdered detergent composition.

where the size of the particles is generally in the range of 0.5 to 1.5mm.

Example 2

The effect of silicate on cake strength

The cake strength of the anti-foam material made according to Example 1 was compared to an anti-foam material made in the same way but with the silicate omitted.

The test method uses a fixed volume of agglomerate which has been compressed into a free standing cylindrical cake. The force needed to collapse this cake is measured on a force gauge driven into the cake. The force required to collapse the cake is a measure of the potential for the agglomerate to form cakes during preparation or on storage.

Approximately 200g of representative sample was placed into a hollow cylinder and a solid cylinder was placed inside the hollow cylinder on top of the sample. A 10kg weight was applied and left for 2 minutes. Carefully the weight, the cylinder and the hollow cylinder were removed from the sample, leaving a cake of the agglomerate. A force gauge was then driven into the cake until it collapsed. The force in kg required to break the cake was noted.

Table 1 shows the cake strength of the anti-foam agent with and without silicate expressed in kg force.

TABLE 1

WITH SILICATE	WITHOUT SILICATE
0	1.91

Example 3

The effect of adding anti-foam material

The effect of adding the anti-foam material made according to the example was tested using the two detergent compositions shown in Table 2.

TABLE 2

DETERGENT FORMULATION

	1	2
SURFACTANTS		
Linear alkyl benzene sulphonate	8	8
C_{14} fatty acid-7 ethoxylate groups	2	5
C_{14} fatty acid-Alkylsulphate	3	3
BUILDERS		
STPP Sodium tripolyphosphate	30	
Zeolite A		25
Polyacrylic-acid		5
BLEACH		
Perboratemonohydrate	15	15
TAED	3	3
ENZYMES		
Enzymes (Savinase)	0.5	0.5
BUFFER		
Na2CO3	15	11
Silicate	5	6
SUDS SUPPRESSANT		
ANTI-REDEPOSITION AGENT / CHELANT		
Carboxymethylcellulose	0.5	0.5
EDTA	2	2
Phosphonate	0.6	0.6
FABRIC SOFTENER		
Bentonite	15	15
MISCELLANEOUS		
Brightener	0.2	0.2
Perfume	0.2	0.2

The principle behind the test used is to see how the anti-foam material controls suds during a washing machine cycle. A standard wash cycle is used and the height of the suds viewed through the washing machine window is plotted against time.

76g of test material (detergent +/- suds suppressor) was placed into the washing powder dispenser of a Miele Novotronic™ W820 washing machine. The program was set to cotton wash and the temperature set to 40°C. The suds level was noted at intervals of time and the sud levels graded on a scale of 1 to 6, with 6 indicating a full window on the washing machine.

The results are shown in Table 3 and Figs. 1 and 2.

TABLE 3

SUDS PROFILE

TIME (mins)	FORMULATION ONE: WITH ANIT-FOAM ADDITIVE	FORMULATION ONE: NO ANTI-FOAM ADDITIVE	FORMULATION TWO: WITH ANTI-FOAM ADDITIVE	FORMULATION TWO: ANTI÷FOAM ADDITIVE
1	0.4	2.3	0.1	0.2
5	0.5	6.0	0.2	1.4
10	0.8	6.0	0.2	2.5
15	0.0	6.0	0.5	4.4
20	1.3	6.0	0.5	5.7
25	1.8	6.0	0.7	6.0
30	2.3	6.0	1.0	6.0
35	3.1	6.0	1.2	6.0
40	3.5	6.0	1.5	6.0
45	4.0	6.0	1.7	6.0
50	4.2	6.0	2.0	6.0
55	4.3	6.0	2.5	6.0

6 indicates a full window, test abandoned if suds level over 6

The results clearly show that the anti-foam material of the invention significantly reduces foaming.

Example 4

The effects of the components of the anti-suds material or suds profile

This was tested using compositions based on Example 1 omitting ester and/or silicate.

The suds profile test of Example 3 was repeated using the following detergent.

TABLE 4

COMPOUND	Weight %
Soda Ash	23.6
Sodium Sulphate	35.0
Zeolite	3.5
Linear Alkyl Benzine Sulphonate	5.0
Carboxymethyl Cellulose	0.17

76g of detergent was mixed 8g of anti-foam agent and used in a washing machine at 40°C.

The results are shown in Table 5 and Figure 3.

TABLE 5

SUDS PROFILE
FRESH PRODUCT

TIME (mins)	STANDARD	NO ESTER	NO SILICATE	NO ESTER/NO SILICATE
1	0.3	0.2	0.4	0.4
5	0.5	0.4	0.7	0.8
10	0.9	0.9	0.9	1.1
15	0.2	1.3	1.7	1.7
20	0.4	1.8	2.4	1.9
25	0.5	2.3	4.3	2.3
30	0.8	2.7	5.8	2.7
35	0.9	2.8	6.0	3.2
40	1.1	2.9	6.0	3.4
45	1.1	3.0	6.0	3.8
50	1.2	3.0	6.0	4.7
55	1.3	3.3	6.0	5.4

6 indicates a full window, test abandoned if suds level over 6

The results clearly show that the ester and silicate components individually reduce the suds profile obtained, but the greatest effect is obtained when they are used in combination.

Example 5

The effect of the components of the anti-foam material on aging

The compositions used in Example 4 were artificially aged by boxing in a cardboard box and leaving at room temperature for one week.

The effects on the aging on of the formulation on the suds profile produced is shown in Table 6 and Fig. 4.

TABLE 6

SUDS PROFILE
AGED PRODUCT (1 week)

TIME (mins)	STANDARD	NO ESTER	NO SILICATE	NO ESTER/NO SILICATE
1	0.1	0.2	0.7	0.9
5	0.4	0.4	2	2.4
10	0.7	1.4	4.1	4.7
15	0.6	2.0	4.9	6.4
20	0.8	2.9	5.7	6.0
25	0.7	3.0	5.9	6.0
30	1.0	3.2	6.0	6.0
35	1.0	3.5	6.0	6.0
40	1.2	3.8	6.0	6.0
45	1.4	4.1	6.0	6.0
50	1.7	4.4	6.0	6.0
55	2.1	5.0	6.0	6.0

6 indicates a full window, test abandoned if suds level over 6

The results show that the material with silicate omitted is effected by aging, thus showing that silicate inhibits degradation of the detergent composition.

Example 6

The effect of high silicone content

A premix was made of silicone anti-foam (TP 331), 4.554 Kg and sorbitan monooleate, 4.554 Kg by mixing in a tank. This mix was then blended with the Zeolite A, 28.2 Kg in a high shear mixer. This was then agglomerated with Sodium di-silicate, 6.75 Kg in a high shear mixer and the silicate added by dripping into the mixer.

From the resulting granules 5 Kg were dried in a fluid-bed drier for 45 minutes at 30°C. This resulted in a formulation as follows:

Zeolite 67.05% (28.2 Kg)

TP331 silicone anti-foam 10.83% (4.554 Kg)

Sorbitan monooleate (Crill 4) 10.83% (4.554 Kg)

Sodium disilicate 8.83% (3.71 Kg)

Water balance of 100%

Mean Particle size 720 micron

Density 991.6 g/L

This resulted in a good suds profile using the method of Example 3 with the detergent of Table 4. 4g of anti-foam with 76g of test detergent gave the result as shown in Table

7.

TABLE 7

Time	Suds height
1	0.3
5	0.6
10	0.8
15	0.8
20	0.9
25	0.9
30	1.0
35	1.1
40	1.1
45	1.3
50	1.6
55	1.9

The results show that high silicone concentrations produce good suds suppression.

Example 7

10g of silicone anti-foam (TP 331 was premixed with 10g of Sorbitan monc-oleate (Crill 4). This was then mixed with 90g of Light Soda Ash. This resulted in slight granulation with good white colour granules. The suds testing following the method of Example 6 and gave the following results using 4g of anti-foam in 76g of test detergent tested at 30 C:

time	suds height
1	0.2
5	0.2
10	0.5
15	0.9
20	1.7
25	1.9
30	2.0
35	2.0
40	2.0
45	2.0
50	2.4
55	2.9

Example 8

To assess the effect of bentonite as a carrier 10g of anti-foam (TP 331) was mixed with 10g of ethoxy sorbitan mono-oleate (Crillet 4 super). The resulting mixture was then mixed with 90g of bentonite (QPC 300). This resulted in a relatively free flowing powder. 4g of anti-foam in 76g of test detergent tested at 40 C gave the following suds profile:

time	suds height
1	0.2
5	0.5
10	0.9
15	1.4
20	2.5
25	3.0
30	3.0
35	3.0
40	3.4
45	3.7
50	3.9

CLAIMS:

1. A granular anti-foam material comprising a carrier, a silicone anti-foam agent, and a fatty acid ester of a polyhydric alcohol.

2. A granular anti-foam material according to claim 1 additionally comprising a silicate.

3. A granular anti-foam material according to claim 1 or claim 2, wherein the carrier is an aluminosilicate.

4. A granular anti-foam material according to claims 1 to 3 having a surface coating of aluminosilicate dust.

5. A granular anti-foam material according to claim 3 or claim 4, wherein the aluminosilicate is a zeolite.

6. A granular anti-foam material according to any preceding claim, wherein the fatty acid component of the ester is unsaturated.

7. A granular anti-foam material according to claim 6, wherein the fatty acid component is a C_{10} to C_{26} unsaturated fatty acid.

8. A granular anti-foam material according to claim 7 wherein the fatty acid component is oleic acid.

9. A granular anti-foam material according to any preceding claim wherein the alcohol is a triol.

10. A granular anti-foam material according to any preceding claim wherein the ester is liquid at ambient temperature and has an HLB value of 2 to 7.

11. A granular anti-foam material according to claim 10 wherein said HLB value is about 4 to 5.

12. A granular anti-foam material according to claim 10 wherein the ester is sorbitan monooleate.

13. A granular anti-foam material according to claim 1 wherein the carrier is zeolite A or a cellulose-based material.

14. A granular anti-foam material according to claims 2 to 13 wherein the silicate has a SiO_2:Na_2O ratio of 1.5 to 2.5.

15. A granular anti-foam material according to claim 14 wherein the silicate is sodium disilicate.

16. A granular anti-foam material according to any of claims 3 to 14 which contains from 40 to 80% by weight of the aluminosilicate.

17. A granular anti-foam material according to claim 16, wherein the anti-foam material contains about 60% by weight of the aluminosilicate.

18. A granular anti-foam material according to any preceding claim wherein the whole composition contains from about 3 to 18% by weight of the silicone anti-foam agent and, independently, from about 3 to 18% by weight of the fatty acid ester.

19. A granular anti-foam material according to claim 18 wherein the whole composition contains from about 7 to 11% by weight of silicone anti-foam agent and independently

about 7 to 11% by weight of the fatty acid ester.

20. An anti-foam material according to any of the preceding claims containing about the same proportions by weight of the silicone anti-foam agent and the fatty acid ester.

21. A granular anti-foam material according to claim 20 containing about 7 to 11% by weight of the silicone anti-foam agent and about 7 to 11% by weight of the fatty acid ester.

22. A granular anti-foam material according to claim 19 or 21 containing about 10% by weight of the silicone anti-foam agent and about 10% by weight of the fatty acid ester.

23. A granular anti-foam material according to claim 4 wherein the aluminosilicate dust is zeolite A and is present in an amount of from 3 to 16% by weight of the anti-foam material.

24. A granular anti-foam material according to claim 23, wherein the zeolite A coating is present in an amount of about 10% by weight of the anti-foam material.

25. A detergent composition containing a granular anti-foam material according to any preceding claim.

26. A detergent composition according to claim 25 for use in a front loading washing machine.

27. A method of preparing a granular anti-foam material for detergent compositions comprising the steps of:

(a) mixing a fatty acid ester of a polyhydric alcohol with a silicone anti-foam agent;

(b) mixing the mixture produced in step (a) with a carrier;

(c) mixing the mixture produced in step (b) with a silicate; and

(d) drying the product produced in step (c).

28. A method of preparing a granular anti-foam material according to claim 27, wherein the mixing step (b) utilises a high shear mixer.

29. A method of preparing a granular anti-foam material according to claim 27 or 28, wherein the mixing step (c) uses a high shear granulator.

30. A method of preparing a granular anti-foam material according to claims 25 to 29, wherein the drying step (d) is carried out using a fluid bed dryer.

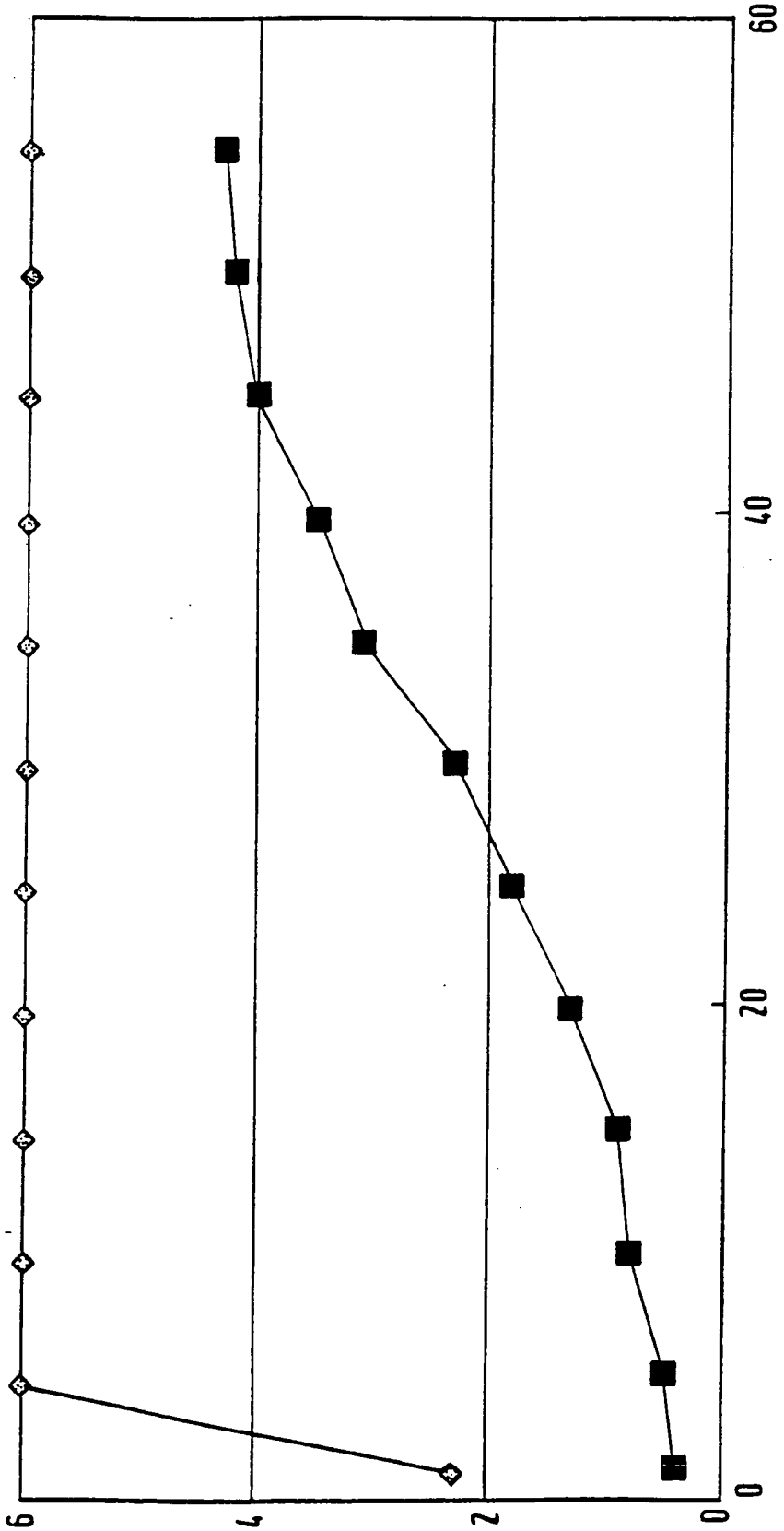


Fig.1.

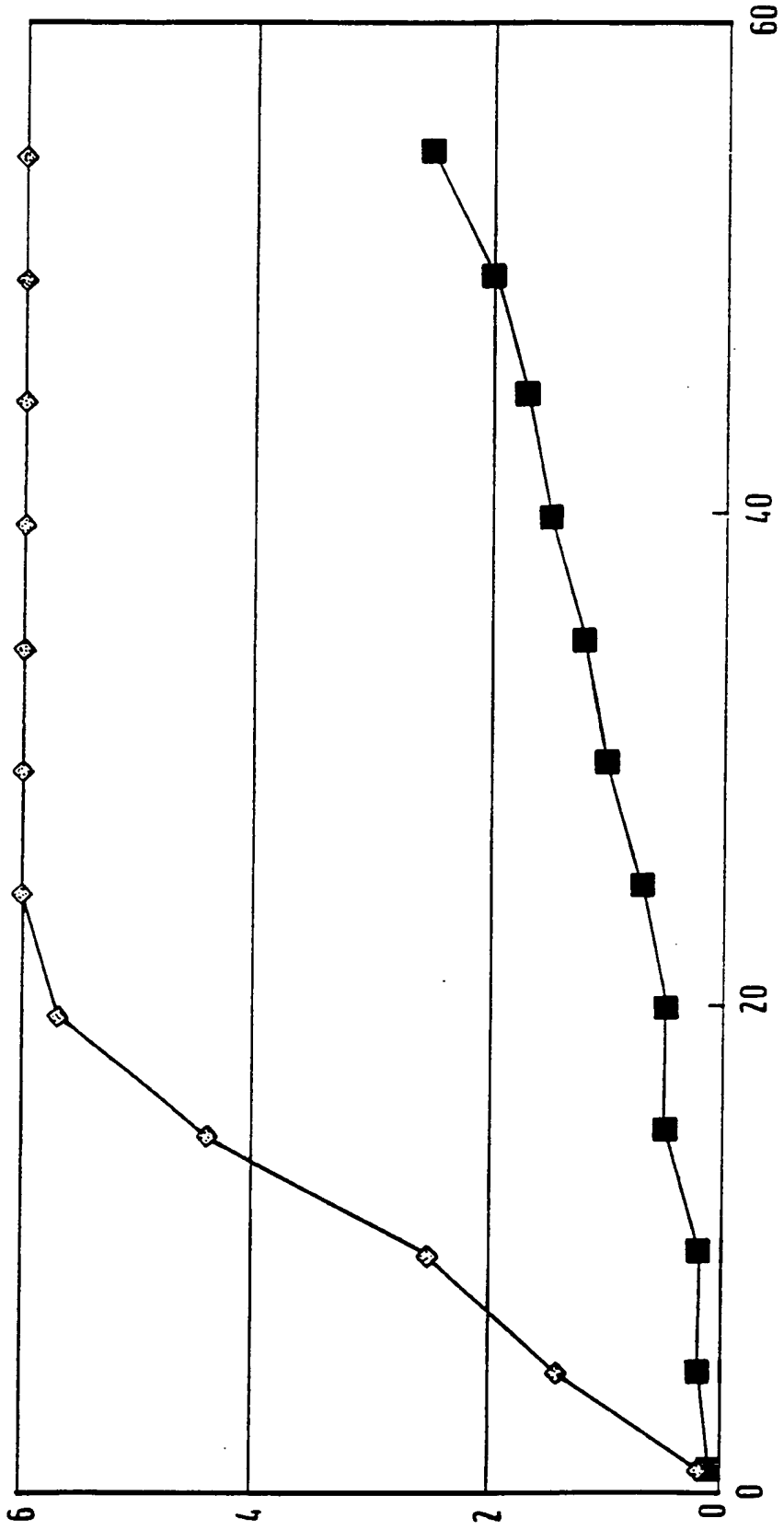


Fig.2.

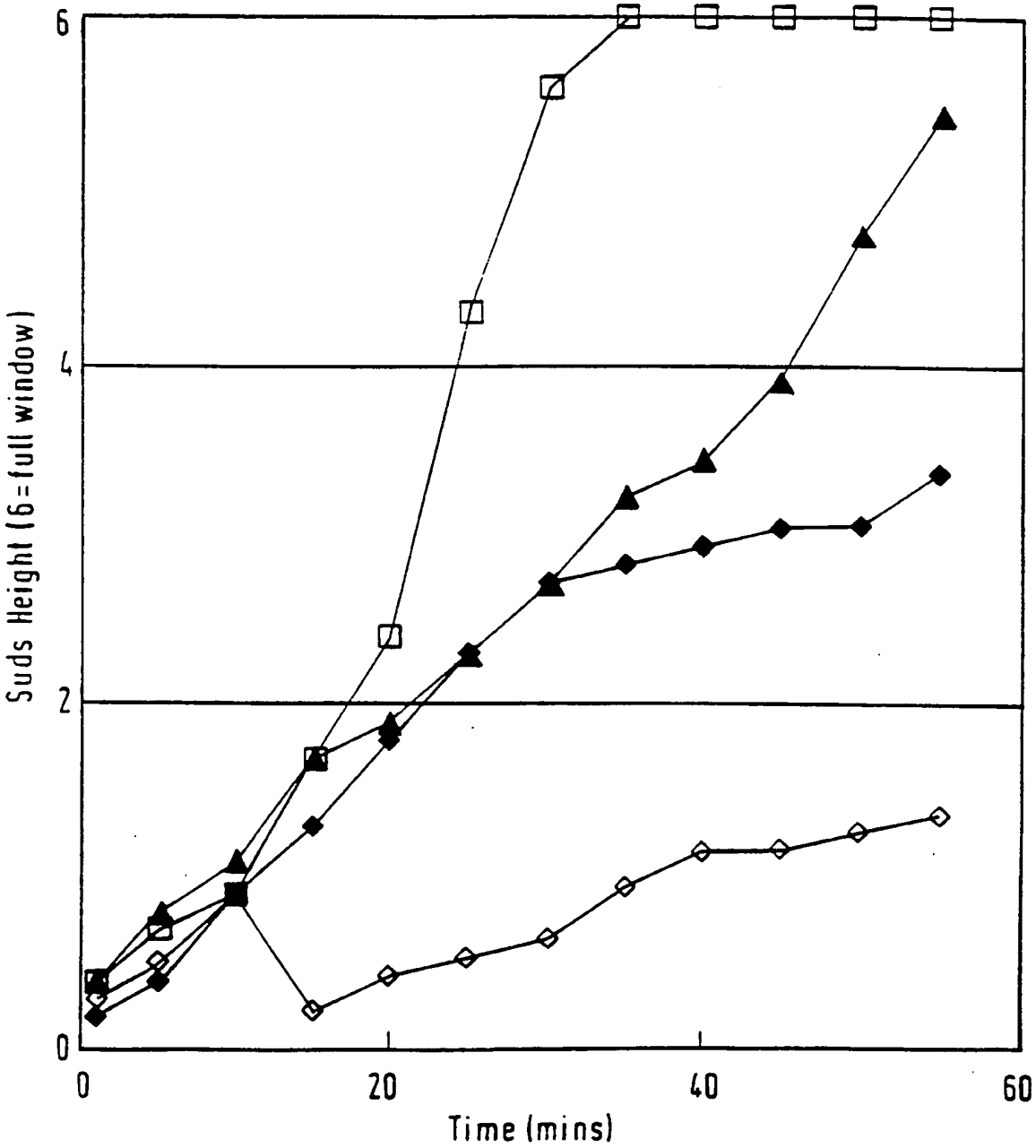


Fig.3.

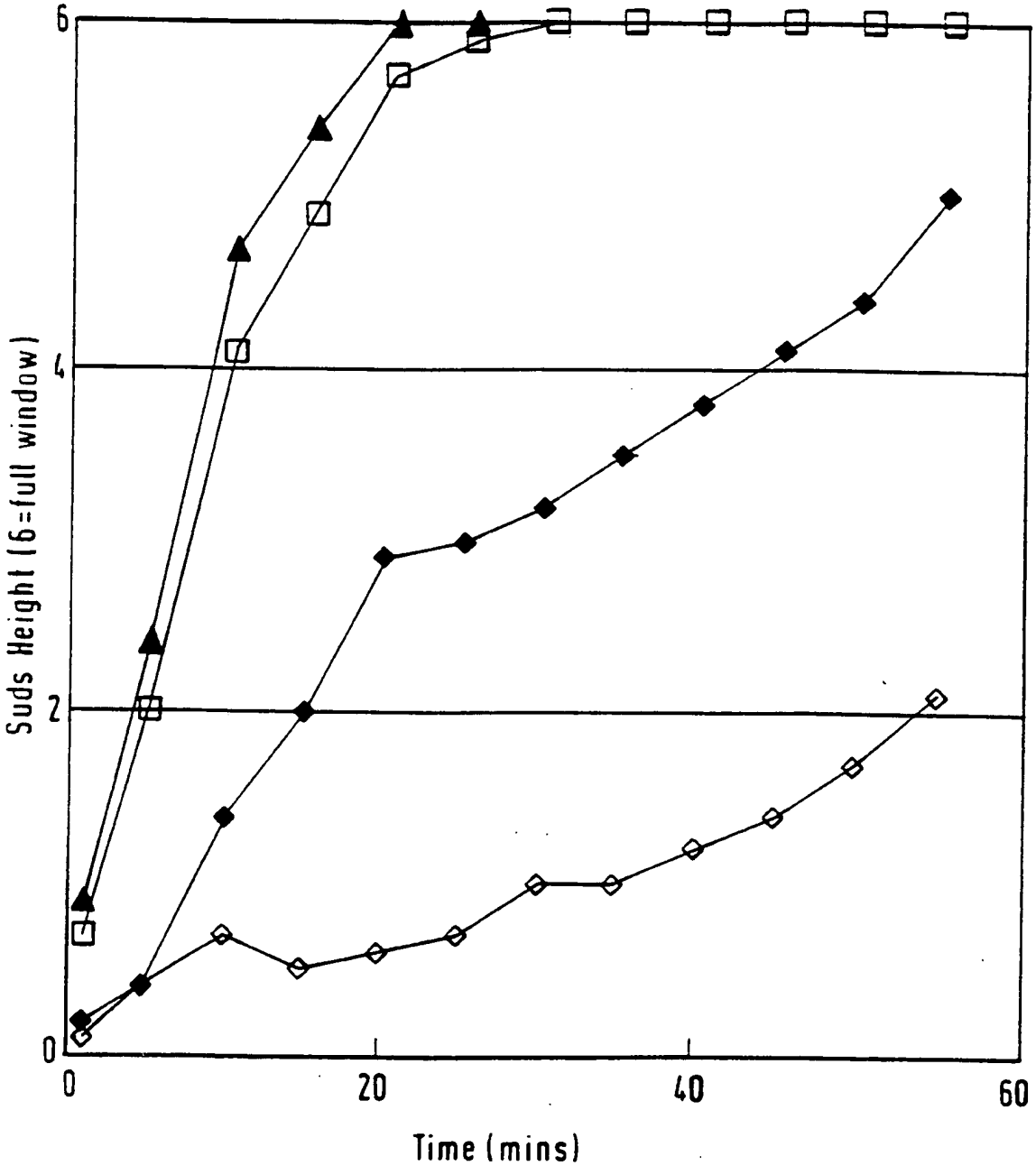


Fig.4.

INTERNATIONAL SEARCH REPORT

Interr al Application No
[redacted]GB 96/01024

A. CLASSIFICATION OF SUB[redacted]MATTER
IPC 6 B01D19/04 C11D3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 517 298 (P & G) 9 December 1992 see page 1, line 41 - page 4, line 46; claims 1-13	1-3,5-7, 9,13, 16-19,25
X	EP,A,0 496 510 (DOW CORNING) 29 July 1992 see claims 1-10	1,9,25
X	EP,A,0 210 731 (DOW CORNING) 4 February 1987 see claims 1-8	1,9,25
X	EP,A,0 206 522 (UNILEVER) 30 December 1986 see claims 1-23	1,9,25

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
31 July 1996	06. 08. 96

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

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Interr ...al Application No
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